CHARGE NUMBER: 2308

PROGRAM TITLE: Room Aroma Component Evaluation

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PROJECT LEADER: A. G. Kallianos

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I. SIDESTREAM SMOKE EVALUATIONS*

Pursuant to studies leading to a determination of the threshold level of WS-14 in sidestream smoke, we have obtained subjective descriptions of the relative characteristics of sidestream smoke from Northwind and Merit cigarettes. The assessments were made utilizing the room aroma evaluation apparatus. The panel, consisting of twenty people, was able to distinguish subjectively the two sidestreams of smoke over a wide range of concentrations. And, although the level of recognition of either cigarette increased as its relative concentration increased, the quality of odor did not appear to change very much, except that WS cooling becomes more obvious at higher concentrations.

The composite of sensations derived when sniffing sidestream smoke include odor, pungency, and irritation of the eyes and mucous membranes. In general, the panel found sidestream smoke from Northwind cigarettes to be less objectionable than that from Merit. Less smokey, less pungent, fresher, cooler, and even less irritating were the adjectives used to describe Northwind sidestream smoke relative to Merit. At high concentrations, where WS cooling is obviously apparent, a tingling, penetrating sensation was perceived in the throat with a cooling, stinging sensation in the eyes and sinus cavities. These were perceived as being "menthol" related and were not judged as objectionable. An overall change in the ammoniacal character of the smoke was noted providing a freshness reminiscent of "Windex" window cleaner.

The WS threshold measurements are nearing completion. Comparative studies with sidestream smoke from menthol cigarettes will follow.

II. COOKED FLAVORS

Work reported at this time relates to studies conducted by several groups within R & D in attempts to establish analytical specifications for cooked flavors and to develop procedures for quality control purposes. The complexity of the cooked flavor mixture and the limited knowledge regarding compositions and "active" flavor principles have prompted us to consider several procedures in this pursuit. A program has been outlined (memorandum by A. G. Kallianos to F. L. Daylor, August 3, 1981) to evaluate methods giving specific information on volatile and non-volatile components as well as methods which may lack specificity but could yield usable information.

Preliminary work has been conducted with nine samples. Six of these were considered acceptable on the basis of flavor evaluations and three were considered unacceptable, although some questions arose on the validity of these designations.

Mr. H. Grubbs and his group examined the samples using HPLC in a reverse phase, without extraction or pre-analysis workup. Although tentative, their conclusion was that "fingerprint" chromatograms may provide information on the acceptability of a particular sample.

Ether extractable materials from these samples were prepared by D. Douglas and chromatographed on a fused silica glass capillary column coated with Carbowax 20M. His tentative conclusions, reported in a memorandum dated September 3, 1981 to R. Comes, state that a peak identified as isovaleric acid relates quantitatively to the acceptability of the samples, and that a similar correlation existed with a peak identified as valeric acid. Reported in that memorandum were also tentative identifications of methyl-, dimethyl-, and trimethylpyrazines. Responsibility for further work with volatile materials using high resolution gas chromatography was transferred to the Analtyical Division.

We evaluated methylene chloride extractables from the nine samples, spiked with an internal standard, by gas chromatography using a series of packed columns. Although our chromatograms provided low resolution of materials, they showed delineations between acceptable and unacceptable samples by variations in the relative intensities of several peaks. Importantly though, we found that the intensities of many peaks could be influenced by the pH of the cooked flavor samples. With no apparent relationships between acceptable and unacceptable, the pH of the nine samples varied from 4.58 to 6.52. Adjustments of the pH of the samples to a common pH appeared to sharpen the delineation between acceptable and unacceptable samples on the basis of relative intensities of several peaks.

Aliquots of methylene chloride extractables from an acceptable sample were dissolved in ethanol and injected into cigarettes for flavor evaluation. Extractables were also obtained from aliquots of this sample after pH adjustments. In these instances, the pH was adjusted by a whole unit, both above and below the extant level. Aliquots of these extracts were injected into cigarettes for flavor evaluations. All three samples imparted desirable flavor smoking qualities to the cigarettes. Smoking evaluation of non-dialyzable pigment recovered from a cooked flavor preparation revealed undesirable flavor effects.

Early in the course of this work, we recognized the need for a more extensive array of samples, both acceptable and unacceptable, to evaluate variations, ranges, and the effects of different variables in the preparation of cooked flavors on the analytical outcome. For this purpose, Mrs. Louise Wu has prepared fourteen new samples; some expected to be acceptable and several intentionally "ruined." These samples are currently under investigation by various analytical procedures and subjective assessments. Specific gravity determinations and pH measurements have been completed on all of these samples. Neither specific gravity nor pH appear to correlate with acceptability, although pH measurements appear to provide a consistent reflection of the history of the samples. Sugar analysis and sensory evaluations have also been completed for seven of these samples.

Working with these seven samples, C. Kroustalis and F. Hsu have obtained ethyl acetate extracts which they have independently chromatographed using high resolution techniques. Based on GC retention times, Kroustalis has tentatively identified pyrazine, 2-methyl-pyrazine, 2,3-, 2,5-, and 2,6-dimethylpyrazines, 2,3,5-trimethylpyrazine, isovaleric acid, n-valeric acid, 2-ethyl-3,5- and 3,6-dimethyl-pyrazines and possibly acetylpyrazine. Additionally, he has found large variations

on repeated scans within acceptable as well as intentionally ruined samples. However, there are indications of quantitative differences between acceptable and "ruined" samples. Interestingly, he observed that the ethyl acetate extracts of ruined samples were devoid of color. Hsu has obtained 35 profiles by replicate analyses of the seven samples using high resolution gas chromatography. Seventy-three peaks from each profile were selected as input to factor (BMDP4M) and discriminant (BMDP7M) analyses to separate pattern plots. Data analysis is in progress.

Gas chromatographic analysis of methylene chloride extracts from the seven samples on packed columns revealed rather complex chromatograms. These are being examined visually for significant distinguishing features.

Work on this aspect of the project will continue by the several groups.

III. REFERENCES

*1. A. G. Kallianos, Notebook Number 7619, pp. 8, 9, 10.

2. B. T. Joyner, Notebook Number 7605.

3. L. Wu, Notebook Number 7639.

4. C. Kroustalis, Notebook Number 7274.

5. F. Hsu, Notebook Number 7576.

A. G. Kallianos

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